(obtained using an F_2 laser source) may be used for future microelectronics fabrication using 0.100 μm or less design rules. The opacity of traditional UV and deep-UV organic photoresists at 193 nm precludes their use in single-layer schemes at this wavelength. Recently new photoresist compositions comprising cycloolefin-maleic anhydride alternating copolymers have been shown to be useful for imaging of semiconductors at 193 nm (see F. M. Houlihan et al., Macromolecules, 30, pages 6517-6534 (1997); T. Wallow et al., SPIE, Vol. 2724, pages 355-364; and F. M. Houlihan et al., Journal of Photopolymer Science and Technology, 10, No. 3, pages 511-520 (1997)).

Comb polymers are a particular class of branched polymers wherein one or more branch (polymer) segments are linked along a linear (polymer) backbone segment. Comb polymers may also be described as linear polymers with polymeric arms. Such polymers typically are prepared by copolymerizing a conventional monomer with a macromer. Macromers are defined by Kawakami in the "Encyclopedia Of Polymer Science And Engineering", Vol. 9, pp. 195-204 (John Wiley & Sons, New York, 1987) to be polymers of molecular weight ranging from several hundred to tens of thousands, with a functional group at the end that can further polymerize, such as an ethylenic, an epoxy, a dicarboxylic acid, a diol or a diamino group. U.S. Patent 5,061,602 discloses the use of such a polymer as a binding agent in a negative-working photopolymerizable material suitable for producing printing forms or resist patterns. The polymer binder disclosed consists of a film-forming copolymer that has a multi-phase morphology where at least one phase has a glass transition temperature below room temperature and at least one other phase has a glass transition temperature above room temperature. The copolymer has an average molecular weight (weight average) of more than 10,000, and is produced using an ethylenically unsaturated macromer with an average molecular weight (weight average) of 1000 to 100,000. The use of graft (comb) copolymers having acid functionality in certain negative-working photosensitive compositions, such as solder masks, has published (see PCT International Publication No. WO92/15628.

M. Yamana et al., Deblocking Reaction of Chemically Amplified ArF Positive Resists, PROC. SPIE - INT. SOC. OPT. ENG., Vol. 3333, No. 1, pages 32-42 (June 1998) discloses deblocking reaction mechanisms and lithographic performance in chemically amplified positive ArF resists consisting of triphenylsulfonium triflate as an acid generator and the copolymer poly(carboxy-tetracyclododecyl methacrylate$_{70}$-*co*-tetrahydropyranylcarboxy-tetracyclododecyl methacrylate$_{30}$). EP 0 473 547 A (CIBA-GEIGY AG 4 March 1992) discloses certain olefinically unsaturated onium salts which can be polymerized and used as

photosensitive copolymers in photoresist compositions. The photosensitive copolymers disclosed include branch copolymers containing protected acid groups and acid-generating groups.

There is a critical need though for other novel resist compositions for use at 193 nm or lower, and particularly at 157 nm, that have not only high transparency at these short wavelengths but also other suitable key properties, including good plasma etch resistance and adhesive properties. This invention addresses this critical need by providing new advantageous compositions and associated processes, comprising graft (comb) copolymers, which have these key properties.

SUMMARY OF THE INVENTION

The present invention comprises:

(A) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight (M_n) of least 1000.

(B) at least one photoacid generator.

In another embodiment, the invention is a positive photoresist as described supra wherein the photoacid generator is covalently bonded to the branched polymer. The invention also includes a process for preparing a photoresist image on a substrate comprising, in order:

(W) applying a photoresist composition on a substrate, wherein the photoresist composition comprises:

(a) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branched polymer contains sufficient functionality to render the photoresist developable to afford a relief image, upon imagewise exposure to violet or ultraviolet radiation and subsequent heating, and wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight (M_n) of at least 1000;

(b) at least one photoacid generator; and

(c) a solvent;

(X) drying the coated photoresist composition to remove solvent and thereby to form a photoresist layer on the substrate;

(Y) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

(Z) developing the exposed photoresist layer having imaged and non-imaged areas to form the relief image on the substrate.

The photoresist compositions of this invention have a particularly good balance of desirable properties, including high transparency to near, far, and extreme ultraviolet light, high plasma etch resistance, and projected high resolution characteristics suitable for microelectronic device fabrication.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of absorbance (μm^{-1}) versus wavelength (nm) in the UV region for corresponding random, block, and graft copolymers having the same or similar comonomer compositions.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Each photosensitive composition of this invention contains a branched polymer, also known as a comb polymer, which contains protected acid groups. The branched polymer has branch segments, known as polymer arms, of limited molecular weight and limited weight ratio relative to a linear backbone segment.

Process Steps

Imagewise Exposure

The photoresist compositions of this invention are sensitive in the ultraviolet region of the electromagnetic spectrum and especially to those wavelengths $\leq$367 nm. Imagewise exposure of the resist compositions of this invention can be done at many different UV wavelengths including, but not limited to, 365 nm, 248 nm, 193 nm, 157 nm, and lower wavelengths. Imagewise exposure is preferable done with ultraviolet light of 248 nm, 193 nm, 157 nm, or lower wavelenths; is more preferable done with ultraviolet light of 193 nm, 157 nm, or lower wavelengths; and is still more preferably done with ultraviolet light of 157 nm or lower wavelengths. Imagewise exposure can either be done digitally with a laser or equivalent device or non-digitally with use of a photomask. Suitable laser devices for digital imaging of the compositions of this invention include, but are not limited to, an argon-fluorine excimer laser with UV output at 193 nm, a krypton-fluorine excimer laser with UV output at 248 nm, and a fluorine (F2) laser with output at 157 nm. Since, as discussed supra, use of UV light of lower wavelength for imagewise exposure corresponds to higher resolution (lower resolution limit), the use of a lower wavelength (e.g., 193 nm or 157 nm or lower) is generally preferred over use of a higher wavelength (e.g., 248 nm or higher). Specifically, imaging at 157 nm is preferred over imageing at 193 nm for this reason.

Development

The graft copolymers in the photoresists of this invention must contain sufficient functionality for development following imagewise exposure to UV light. Preferably, the functionality is acid or protected acid such that aqueous development is possible using a basic developer such as sodium hydroxide solution, potassium hydroxide solution, or ammonium hydroxide solution. Some preferred graft copolymers in the resist compositions of this invention are protected acid-containing copolymers comprised of at least one acid-containing monomer of structural unit:

$$(\text{—}CH_2\text{—}\overset{\displaystyle E^1}{\underset{\displaystyle E^2}{\overset{|}{\underset{|}{C}}}}\text{—})$$

in which E^1 is H or C_1-C_{12} alkyl; E^2 is CO_2, E^3 is SO_3E, or other acidic functional group; and E and E^3 are H or C_1-C_{12} alkyl, which is unsubstituted or hydroxyl-substituted. Alkyl groups can contain one to twelve carbon atoms and preferably